2. What are the kinetics of gasification and combustion?

3. What are the effects on gasification of -- feed stock, product gases, bed height, steam preheat, superficial steam velocity, ash content in melt and others?

4. Can coal ash be removed from the melt and the sodium recovered economically?

Some of the answers on gasification and the problems of getting the answers are presented in this report. Other topics will be discussed in subsequent reports.

II. EXPERIMENTAL

A. Apparatus

Most of the experimental work has been concerned with rates of gasification. The equipment for this centers about the reactor, which based upon earlier molten salt research, was made out of 2-inch I.D. Inconel 600 pipe, schedule 40, 26 inches long. A thermowell made out of ¼-inch Inconel tubing entered at the bottom of the reactor. A ¼-inch Inconel tube for steam and nitrogen entered from the top and extended to within ½ inch of the bottom of the reactor. Also affixed to the top of the reactor was a ½-inch pipe with two quick opening ball type valves which served as a lock hopper for introduction of the carbonaceous solid as 12/20 mesh material. Gases exited near the top of the reactor into ¼-inch pipe which connected to a 4-way tee through which a horizontal and a vertical drill sealed by Conax fittings could be employed to keep the exit line open. A water condenser was followed by a separator, a back pressure regulator, sample taps for gas chromatography, and a wet test meter.

Water was pumped using a Ruska positive displacement pump or Lapp diaphragm LS-10 and 20 pumps. This water with a nitrogen sweep went into a 40-inch long steam generator made out of 1-inch pipe and appropriately wound with heating wire. A superheater, made out of 20 feet of ¼-inch tubing in a coil 10 inches long, employed a 12-inch long furnace. The outlet was connected to the ¼-inch tubing that went internally to the bottom of the reactor. All exposed piping from the generator to the reactor and the hopper to the reactor was wound with covered resistance wire. Nitrogen and other gases were delivered with conventional equipment through calibrated rotameters. The 90% steam-10% nitrogen stream was normally fed at 0.5 ft/sec superficial gas velocity in the reactor.

A 24-inch long Kanthal furnace of 2.75-inch diameter served to heat the reactor. All thermocouples were chromel-alumel. Multiple point recorders were used. Gases were analyzed using a partitioner

to obtain N_2, CO_2, CO and hydrogen by difference. Mass spectrometry and other gas chromatography equipment were utilized when necessary.

B.   Procedure

Operation consisted in introduction normally of 414 grams of pure, dense sodium carbonate which was melted and brought to the appropriate temperature with a flow of nitrogen through the steam inlet. This amount of molten salt measured four inches in depth under quiescent conditions. Steam rate was then set and the carbonaceous solid introduced. Sufficient solid was charged, based upon its total carbon content, to give 4% by weight of carbon in the melt initially. Collection of an aliquot of the gas stream was made to get the average composition for the first five minutes. Product gas was analyzed at intervals of five and ten minutes until the run was terminated. Total carbon gasified per five minute or other interval was calculated and the percent carbon remaining at each time reading was used to plot first-order kinetics.

First-order kinetics was found to satisfy the data at least to 50% carbon consumption and in many of the runs to 90%. Although some deviations have occurred, it has been found that this serves as an excellent method for interpretation of the data. From the half life, the specific reaction rate constant is obtained. In order to give this more illustrative significance, it has been converted into pounds of carbon gasified per hour per cubic foot of molten salt charged when 4% carbon is present in the melt.

High volatile bituminous coal from Island Creek No. 27 mine, Holden, West Virginia, was used. The proximate analysis was: 1.31% water, 37.3% volatile matter, 57.6% fixed carbon and 3.8% ash. The ultimate analysis, on a dry basis, was 83.6% carbon, 5.14% hydrogen, 1.48% nitrogen, 0.66% sulfur, 5.27% oxygen and 3.85% ash.

III.   RESULTS

This report presents the initial studies considered of major importance to the overall process. It is planned that more intensive correlations of the data will be made at a later date.

A.   Gasification Studies -- Effect of Variables

1.   Temperature

The gasification rate at atmospheric pressure at 0.5 ft/sec superficial gas velocity was determined for bituminous coal at three temperature levels. The results are shown in the following tabulation.

Temperature - °F	lb C Gasified/hr/CF
1740	6.5
1840	15.2
1940	33

The jumps in gasification rate with increasing temperature are high and give an apparent activation energy of 50 kilocalories.

2. Pressure

The effect of steam pressure was determined with 30% steam in nitrogen at 1 atmosphere and with 90% steam in nitrogen at 1, 2, 3, 4 and 10 atmospheres. The data have been obtained from runs using bituminous coal, cokes derived from this coal by coking to 1110°F (Coke II) and to 1740°F (Cokes III and IV). Initial runs were made at 1840°F but the high gasification rates decreased the accuracy as shown by scatter in the points for the top curve in Figure 1. Dropping the melt temperature to 1740°F gave an excellent series of points as depicted in the bottom curve of Figure 1. All these runs were made at 0.5 ft/sec superficial gas velocity with a 4-inch bed of molten sodium carbonate and at an initial concentration of 4% carbon in the bed.

There appears to be a linear relationship between the logarithm of the rate and of the steam pressure above one atmosphere which allows a reasonable extrapolation to the desired commercial pressure of 400 psi. For the conditions given, rates of 35 and 66 pounds of carbon gasified per hour per cubic foot of melt at 1740°F and 1840°F, respectively, appear possible at 400 psia. Runs at higher pressures will be made in a pilot plant unit now being designed.

3. Bed Height

The effect of the height of the molten salt bed on the kinetics is of importance for commercial design which at the present calls for bed heights of 10 to 20 feet. Ideally for ease of design, one would like to have no effect of bed height on the kinetics of gasification. Physical limitations of the test equipment have allowed only a limited amount of evidence to be obtained in this area.

The effect of bed height was studied from 3 to 8 inches in the 2-inch diameter reactor. The results at 3, 4 and 6 inches are shown in Figure 2. Conditions for these runs are given in the figure. Adjustment of the position of the reactor in the furnace allowed identical temperature profiles to be obtained for 3 to 6-inch beds but not with the 8-inch high bed.
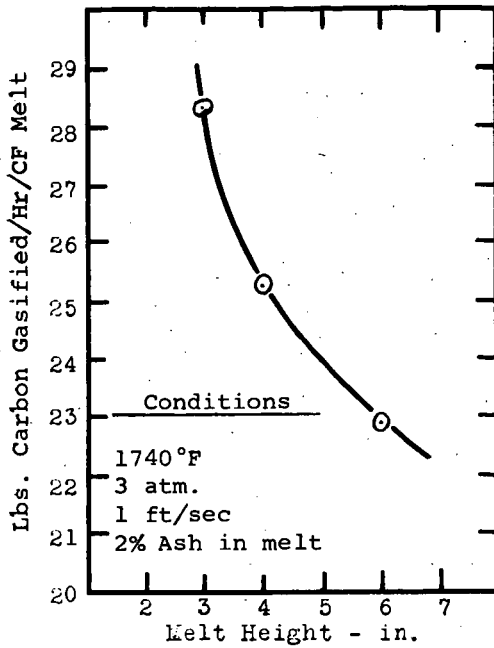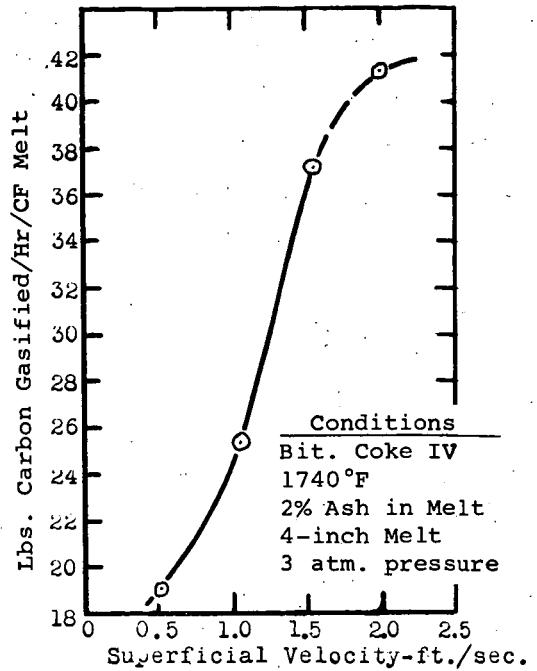
Fig.2 - Melt Height vs. Rate

Fig.3 - Velocity vs. Rate
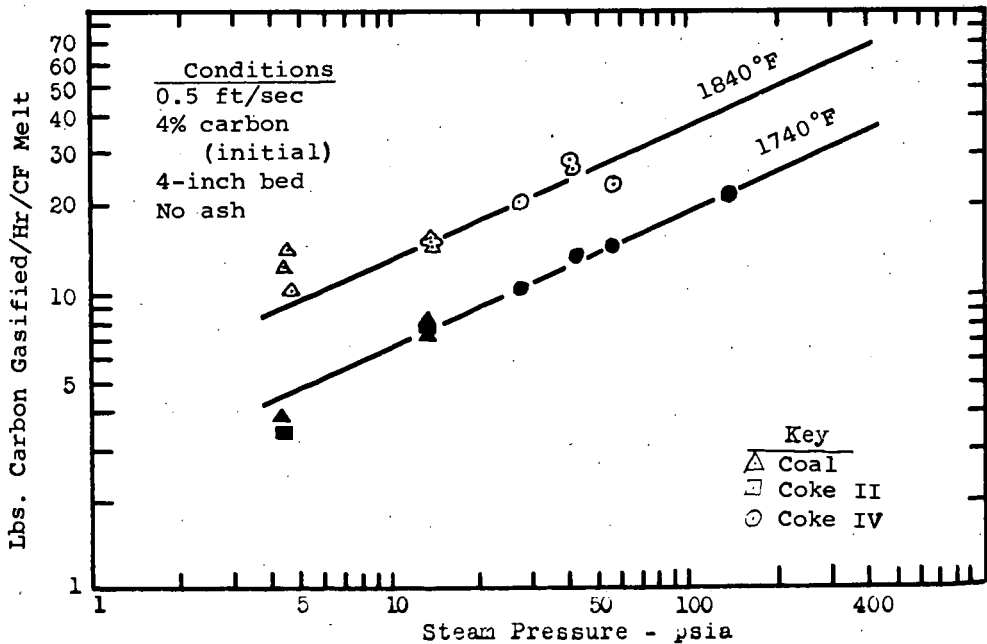
Fig.1 - Effect of Steam Pressure on Gasification Rate

A significant effect of bed height on gasification rate was obtained in the two-inch diameter reactor. It was concluded that this height effect must be due to poorer contact of carbon and steam with increasing height. Size of steam bubbles and distribution of carbon are the principal variables. The latter appears most suspect at this time. It is believed that larger diameter reactors will allow better mixing to be achieved and thus lessen the effect observed here. Further evaluation must await construction of pilot plant equipment.

4. Superficial Steam Velocity

Original adoption of 0.5 ft/sec superficial steam and nitrogen velocity was based upon simulated visual experiments with aqueous zinc chloride system of 2 gr/cc density and charcoal which showed excellent mixing at 0.25 ft/sec and higher velocities. The results of a separate study under gasification conditions are shown in Figure 3. The run at 2 ft/sec taxed the steam generating and condensing system as well as the heat supply from the Kanthal furnace. Temperature dropped from 1740° to 1710°F in the initial part of the run and required a correction back to 1740°F. Thus the dashed part of the curve in Figure 3 is an adjusted value. It does appear that the rate levels off around 2 ft/sec.

The velocity effect very definitely indicates that this system is sensitive to mixing. It appears to confirm the conclusions reached above in the study of bed height.

5. Ash Content in Melt

Normally, operation has been with non-ash containing melts of sodium carbonate because of greater ease of removal by washing and less corrosion on the Inconel reactors. In commercial operation, a steady state content of ash will exist in the melt, the concentration of which will depend on viscosity, degree of sodium recovery, etc. The presence of ash increases the tendency of the melt to froth which increases the interfacial area. Comparison of runs containing 10% bituminous coal ash in the melt with non-ash melts at two temperatures, 0.5 ft/sec velocity and 4-inch bed heights are shown in the following tabulation.

Temperature, °F	Gasification Rate - lbs C/hr/CF	
	Non-Ash	10% Ash
1740	7.5	13.6
1840	14.7	31.9

Approximately a twofold enhancement of rate appears due to the presence of ash. The rates of some runs at 1 ft/sec superficial velocity without ash are about equivalent to rates for runs with ash at 0.5 ft/sec. Some

runs at 1 ft/sec with ash present showed even slightly higher rates over similar runs without ash. Melts with ash have been maintained under carbon dioxide until near the start of the run to decrease the solubilization of ash components.

6. Miscellaneous

Some initial work on <u>particle size</u> of coal indicated the rate was unchanged in using 40/60 mesh rather than the usual 12/20 mesh coal particles. A poor test with -200 mesh material qualitatively indicated an enhanced rate. More work is planned for this area.

Only very little has been done on variation in <u>feed stock</u>. Bituminous coal and coke derived from this coal appear to react at about the same rate while Renner's Cove lignite showed double the rate. Rates are tabulated below for runs at atmospheric pressure, 0.5 ft/sec velocity and 4-inch melt height.

	Gasification Rate - lbs C/hr/CF	
	1740°F	1840°F
Bituminous Coal	6.5	15.2
Bituminous Coke IV	-	14.8
Renner's Cove Lignite	16.5	27.1

Some concern that gas temperature may have been below melt temperature was caused by the product gas composition indicating equilibrium for the water gas reaction was 200° to 300°F below the melt temperature. Several runs with <u>superheated steam</u> entering the reactor at 1500° to 1600°F had no effect on the rate of gasification. Equilibrium for the water gas reaction is not dictated by the melt temperature alone but by some temperature at the wall before cooling and fixing of the gas composition.

In a preliminary study of the <u>effect of product gases</u> upon rate, 30% steam in hydrogen was found to give about the same rate as 30% steam in nitrogen. Hence, hydrogen had no effect upon the kinetics at atmospheric pressure and 1840°F. Although 30% steam in carbon dioxide led to about a 25% decrease in rate, this is viewed with caution since the difference between two large numbers, 10.60 and 9.53 moles, represents the carbon gasified. Carbon monoxide added to steam (30%) reacted with the steam first.

It is planned that at some future date, studies of combustion, viscosity, sodium recovery and solid carryover will be presented to complete this initial picture.

ACKNOWLEDGMENT

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